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Structure–property relationships in ionic liquids: Influence of branched and cyclic groups on vaporization enthalpies of imidazolium-based ILs

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This paper is dedicated to the memory of Alexander "Xander D. Stanton, a talented and promising young researcher and friend who passed away during the course of this project.

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ABSTRACT

Ionic liquids (ILs) with branched and cyclic substituents are seldom studied in the literature, and as such there are little to no data characterizing their thermophysical properties. ILs with branched and cyclic substituents are just as convenient to synthesize and study as their counterparts with linear substituents, but the effects of these substituents on IL properties are not yet well-defined due to the preference for linear substituents. Standard molar vaporization enthalpies of six imidazolium based ionic liquids [Rmim][NTf_2] with iso-alkyl and cyclic substituents (R = iso-propyl, iso-butyl, sec-butyl, methylcyclopropyl, cyclopentyl and methylcyclohexyl) were derived from quartz-crystal microbalance (QCM) method. Enthalpies of vaporization measured at elevated temperatures have been adjusted to the reference temperature 298 K and tested for consistency by comparison with the homomorphy alkane, alkylbenzenes and alkyl-imidazoles. It was found that vaporization enthalpies of ILs with the iso-alkyl and cyclic groups are generally on the same level within (±2 to 3) kJ · mol^{-1} significantly compared to the analogous ILs with the imidazolium cation substituted with the linear alkyl substituents of the same chain length. These findings are useful for the quick estimation of vaporization enthalpies of various substituted IL cations (e.g. pyrrolidinium, ammonium, pyridinium, etc.).

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1. Introduction

The 1-(*n*-alkyl)-3-methylimidazolium ([$C_n$mim]) cation motif is highly prevalent within the ionic liquid (IL) literature, most likely due to the convenience and low cost of 1-methylimidazole and *n*-alkyl halides as starting materials [1]. However, ILs with 'R' groups composed of C and H atoms featuring branching, cycles and/or π-bonds are entirely feasible, but seldom considered [2–11]. As known from works with neutral molecules, branched or cyclic isomers can present significantly different thermophysical properties [12,13], and such differences between isomers are also expected within ILs. Many of the requisite precursors needed to synthesize such ILs (e.g. benzyl chloride, 2-bromopropane) are readily available. Yet, interest in the effects of non-linear hydrocarbon substituents on imidazolium cations has been limited over the past 20 years.

While the lack of studies pertaining to characterization of ILs with branched or cyclic substituents has been obvious to those who have worked within the field for some time, in preparation of this manuscript, we became interested as to exactly what extent ILs with substituents that featured branching, cycles or π-bonds have been explored relative to their *n*-alkyl analogues. To attempt to quantify these trends, structural searches for various imidazolium cations with the bistriflimide ([NTf_2]) anion were performed using SciFinder™. Results for each IL of interest were further narrowed by removing patent references, since patents often tend to claim broad structural groups, but this does not necessarily mean that the compound(s) of interest was actually examined within the work leading to the patent. Based on these SciFinder™ structural searches carried out immediately prior to the submission of this article, we noted that that the vast majority of studies relating to imidazolium-based ILs with bistriflimide

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